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METHOD FOR PRODUCING FUEL OIL ADDITIVES
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SPECIFICATION /1*

1. Title

Method For Producing Fuel Oil Additives

2. Claims

(1) A method for producing fuel oil additives comprising: forming minute particles having a particle size of 200 Å or smaller from an iron compound represented by $MeO \cdot Fe_2O_3$ or $Me(OH)_2 \cdot Fe(OH)_3$ (wherein Me represents a divalent metal, such as Co, Ni, Sn, Ti, Fe, Cr, Mn, Cu, Zn, Ba, Ca, or the like), treating the surface of said particles with oleic acid, and dispersing said minute particles in a solvent to form a colloid.

(2) A method for producing fuel oil additives comprising: combining a deposit formed by adding an alkali to an aqueous solution in which Me^{2+} and Fe^{3+} (wherein Me represents a divalent metal, such as Co, Ni, Sn, Ti, Fe, Cr, Mn, Cu, Zn, Ba, Ca, or the like) are both present with an aqueous solution of oleic acid or an oleic acid salt to treat the deposit; subsequently eliminating water from the treated deposit, thereby obtaining a solid substance; and dispersing the solid substance in a solvent.

(3) A method for producing fuel oil additives comprising: combining a deposit formed by adding an alkali to an aqueous solution in which Me^{2+} and Fe^{3+} (wherein Me represents a divalent metal, such

* Numbers in the margin indicate pagination in the foreign text.

as Co, Ni, Sn, Ti, Fe, Cr, Mn, Cu, Zn, Ba, Ca, or the like) are both present with oleic acid or an oleic acid salt to treat the deposit; subsequently washing the deposit with water; and surface treating it with a hydrophilic anionic active agent or nonionic active agent, thereby dispersing it in water to form a colloid.

3. Detailed Description of the Invention

The present invention pertains to a method for producing fuel oil additives that contain metal compounds in high concentration and that also mix well with fuel oils, typical examples of which include crude oil, heavy oil, kerosene, diesel oil, gasoline, and the like.

Fuel oil additives are, according to their intended uses, known as inhibitors against generation of such harmful substances as sulfur oxides, nitrogen oxides, and the like, sludge separators, de-emulsifying agents, corrosion inhibitors, buildup inhibitors against combustion ashes, etc., combustion accelerators, soot inhibitors, ignition accelerators, cetane boosters, freezing-point depressants, and so forth, and compositions in a solution form or slurry form that are prepared by mixing fine powder of inorganic substances (for /2
example, oxides, chlorides, or the like of inorganic metals or metals) into a solvent or water, together with a dispersant having a surface-active agent as the component, are known as these additives.

The inorganic substances among the components of these fuel oil additives could precipitate and separate during storage, or, when added to fuel oils, these additives could precipitate in pipe sections

or burner sections and clog them or could abrade burner nozzle sections with the organic powder.

In addition, due to poor dispersibility, the inorganic substances in the additives do not make good contact with the components in fuels and burning flames or flue gases; consequently, satisfactory effects as additives cannot be expected from these additives.

The present invention was proposed in view of the aforesaid situation, and it provides a method for producing fuel oil additives that comprises forming an iron compound represented by $MeO \cdot Fe_2O_3$ or $Me(OH)_2 \cdot Fe(OH)_2$ into a fine powder having a particle size of 200 Å or smaller, adsorbing oleic acid to said fine powder, and dispersing the powder in a solvent to form a colloid or a method that comprises combining a deposit formed by adding an alkali to an aqueous solution in which Me^{++} and Fe^{+++} are both present with an aqueous solution of oleic acid or an oleic acid salt to treat the deposit; subsequently eliminating water from the treated deposit, thereby obtaining a solid; and dispersing the solid in a solvent.

Here, Me represents a divalent metal, such as Co, Ni, Sn, Ti, Fe, Cr, Mn, Cu, Zn, Ba, Ca, or the like.

The fine particles or solid thus dispersed have a particle size of 200 Å or smaller, and they are separated from one another in a solvent and dispersed without aggregating, thus assuming a solution form. The solvent used here is not limited to petroleum solvents, such

as kerosene, spindle oil, liquid paraffin, and the like, and non-polar solvents, such as normal heptane, cyclohexane, n-octane, and so forth can also be used.

The colloidal solution thus obtained does not show precipitation of fine particles even after extended time, and it does not separate even under centrifugation or the like. Furthermore, these particles can be diluted to any dilution rate or mixed in high concentration in a solvent. For example, even adding 80% by weight of these particles to kerosene still yields a liquid having fluidity.

As mentioned in the foregoing, when fine particles obtained by treating an iron compound with oleic acid or a solid obtained by treating a deposit from a solution in which Me^{++} and Fe^{+++} are both present are washed with water and subsequently surface-treated with a hydrophilic nonionic active agent or anionic active agent, they are dispersed in water stably and form a colloidal solution, thus making it possible to mix them in any desired amount in water, without precipitation of fine particles.

Fuel oil additives produced by the aforesaid methods are colloidal solutions of $MeO \cdot Fe_2O_3$, $Me(OH)_2 \cdot Fe(OH)_3$, MeO, $Me(OH)_2$, Fe_2O_3, and $Fe(OH)_3$ particles that have been treated with oleic acid, these types of particles being present in the solution singly or in combination. When Me stands for Ba, the additive is effective for inhibiting soot generation. When it stands for Ca, Mg,

or Fe, owing to their high reactivity with sulfur in fuel oils, the additive inhibits the generation of sulfur oxides, nitrogen oxides, and the like. When it represents Co, Cu, Mn, etc., the additive has a combustion promoting effect and inhibits the generation of soot and nitrogen oxides.

In addition, because the dispersed particles have a minute particle size of 200 Å or smaller, they have an extremely large surface area per unit weight and are highly active; as a result, the additives can exhibit high reactivity with active oxygen, sulfur, nitrogen, and other components in fuels, combustion flames, or flue gases and promote the aforesaid effects significantly. Thus, the additives have not only the effect of inhibiting the generation of sulfur oxides, nitrogen oxides, and soot, that is to say, air pollution, but also the effect of inhibiting boiler corrosion caused by the generation of SO_2 and SO_3. Since they contain metal oxides in high concentration, adding them in small quantities can be expected to yield satisfactory effects. When they are added to fuel oils, the compositions disperse and dissolve uniformly, without precipitating or separating, and, consequently, they do not block piping for fuel oils or abrade burners.

Furthermore, it is not necessary to add dispersants, such as surface-active agents and the like, to formulate these additives, and, since the concentration of the metal components in them can be adjusted to any desired level according to the objective and since

they can be stored in high concentration, substantially small-capacity containers and storage tanks can be used; thus, these additives have significant economical effects.

The methods used for the oleic acid treatment in the present invention can be roughly classified into a dry method and wet method.

(1) Dry method

A method that pulverizes and mixes $MeO \cdot Fe_2O_3$ powder together /3 with oleic acid or a salt thereof with a ball mill or the like for an extended time.

(2) Wet method

A method that adds oleic acid or a salt thereof to a component that precipitates when an alkali is added to an aqueous solution in which $Me^{++} \cdot Fe^{+++}$ are both present and stirs to thoroughly mix them, after which water is separated from the solution.

Mixing the particles treated by either one of the aforesaid methods in a lipid solvent, such as kerosene, n-hexane, etc., yields an oil-based fuel oil additive. By washing the particles treated by method (1) or (2) with water and subsequently mixing them into an aqueous solution of a hydrophilic nonionic active agent or anionic active agent, a water-based fuel oil additive can be obtained.

As the aforesaid hydrophilic nonionic active agent, those whose HLB (Hydrophilic Lipophilic Balance) is 12 or larger, such as polyoxyethylene alkylphenol ether, polyoxyethylene alkyl ether, etc., and, as the anionic active agent, alkylbenzene, sodium sulfonate,

sodium alkylsulfate, sodium oleate, and the like can be used, but these are not all that the present invention can use.

As the aforesaid surface-active agent, those whose alkyl groups have 10 or more carbon atoms are effective.

The following presents working examples of the present invention.

Working Example 1 (The dry method)

An admixture of magnetite (300 g) and oleic acid (50 g) was pulverized and mixed with a ball mill continuously for 5 days and then combined with 400 cc kerosene and further pulverized for 10 more days. After the solution thus obtained was left standing for one day, it was filtered by suction, thereby eliminating a residue. The filtrate, from which the residue had been eliminated, was combined with kerosene to set the total amount to 500 cc. This solution did not show any precipitation and separation of the contained components even when it was centrifuged (at 200 rpm for 20 minutes) and thus was found to be a homogeneous solution.

When the concentration of the iron compound in the solution was measured, it was found to be 420 g/L (in terms of Fe_2O_3 quantity). The observation of this solution under a microscope revealed that its particle size was from 50 to 150 Å.

Working Example 2 (The wet method)

An aqueous solution obtained by dissolving 200 g of Mohr's salt $(NH_4)_2 \cdot Fe(SO_4)_2 \cdot 6H_2O$ and 250 g of ferrous ammonium sulfate $Fe(NH_4)(SO_4)_2 \cdot 12\ H_2O$ in 2 L water was combined with 1 L of a 6N aqueous

solution of sodium hydroxide (NaOH) and thoroughly stirred, thereby obtaining a precipitate.

Said precipitate was isolated by filtration and washed with water and subsequently put in 1 L of a 100 g/L aqueous solution of sodium oleate and stirred continuously for 24 hours.

After the stirring, the supernatant was eliminated, and the solution was subjected to vacuum evaporation to evaporate nearly all the water content, after which the resulting product was dried under ordinary pressure for 24 hours, thereby obtaining 240 g of a solid substance in powder form. This powder-form solid substance was added to cyclohexane to set the total amount to 500 mL, thus obtaining a homogeneous solution.

Working Example 3

The powder-form solid substance (200 g) in the aforesaid Working Example 2 prior to the addition of cyclohexane was added to 400 mL of a 5% aqueous solution of sodium dodecylbenzene sulfonate and stirred for 30 minutes at room temperature, thereby obtaining an aqueous solution. This composition did not precipitate even by centrifugation (at 2000 rpm for 20 minutes) and was found to be a homogeneous solution. The Fe content in the composition was 450 g/L in terms of Fe_2O_3.

When the solutions obtained in Working Examples 2 and 3 were examined with an electromicroscope, the sizes of the dispersed particles were in the range of from 80 to 200 Å.

The use of ferrite slags, such as Mn-Zn ferrite, Ni-Zn ferrite, Ba ferrite, and so forth; copper slags; titanium slags; converter slags; waste steel slags; and iron powder, iron pieces, etc., contained in industrial wastewater from foundries, rolling mills, and so forth in place of magnetite used in Working Example 1 yielded similar compositions in solution form, although the yield varied.

In place of the solution of Mohr's salt and ferrous ammonium sulfate used in Working Example 2 and 3, solutions obtained by dissolving the aforesaid ferrites, waste steel slags, iron powder contained in wastewater, or the like in an acid solution at room temperature or by heating can be used in the aforesaid production method.

Furthermore, the use of petroleum solvents, such as diesel oil, spindle oil, liquid paraffin, etc., or the use of nonpolar solvents, such as n-hexane, n-octane, n-dodecane, etc., in place of kerosene /4
or cyclohexane also yielded similar results.

Next, the quantities of soot (measured according to JIS-Z-8808) and nitrogen oxides (measured by the phenol disulfonic acid method in JIS-K-0104) that were generated by burning Bunker C to which had been added the liquid compositions obtained in Working Examples 1 and 3 were measured, and the results are as follows.

The measurements were conducted on flue-gas specimens taken at the air-heater outlet of the following boiler.

The boiler used here was a natural-circulation-type, double-drum, water-tube boiler having a maximum evaporation volume of 40 L/hour, and, using a fuel that was Minama type Bunker C (S minute, 1.0%), it was run with an excess air ratio of 5.3%.

	Additive Amount to Fuel Amount	Nitrogen Oxides (ppm)	Soot (g/Nm^3)
Working Example 1 Composition (Solid content: 45% by weight)	1/1000	115	0.015
	1/2000	130	0.03
Working Example 3 Composition (Solid content: 50% by weight)	1/1000	50	0.01
	1/2000	75	0.02
No Additive	-----	150	0.06

[Translator's Note: The rest of the document is not a part of the patent text.]